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(54) A catalyst and a method for denitrizing nitrogen oxides contained in waste gases

Ein Katalysator und ein Verfahren, Stickoxyde in Abgasen zu entsticken

Un catalyseur et un procédé pour dénitrifier des oxydes d'azote contenus dans des gaz d'échappement

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Description

This invention relates to a catalyst and a method for denitrizing nitrogen oxides contained in waste gases. More particularly, the invention relates to a catalyst for denitrizing nitrogen oxides which retains a high catalytic activity over a long period of operations, and especially, to a catalyst which is resistant to deactivation or poisoning by arsenic compounds such as an arsenic trioxide contained in waste gases together with nitrogen oxides. The invention further relates to a method of denitrizing such waste gases by use of such catalysts.

Denitrizing processes have been recently developed and the processes are industrially carried out in many plants today, to convert noxious nitrogen oxides into innocuous compounds or to remove them from waste gases. In an exemplary denitrizing process, combustion waste gases from coal-fired boilers which contains nitrogen oxides therein is mixed with a reducing gas, and the resultant gas mixture is put into contact with a denitrizing catalyst, thereby to reduce the nitrogen oxides into innocuous compounds. A variety of processes are already known, but a selective catalytic reduction process in which ammonia is used as a reducing gas is said most advantageous from the standpoint of controllability of catalytic reduction reactions of nitrogen oxides and process economy.

Heretofore, the process has been applied only to waste gases which contain no arsenic compounds therein or contain arsenic compounds in such trace amounts as give substantially no influence upon the catalytic activity of denitrizing catalysts. However, a substantial amount of arsenic compounds is occasionally contained in combustion waste gases from coal-fired boilers depending upon the coal used as a fuel, and it has been noted very recently that denitrizing catalysts are deactivated or poisoned within a short period of time by arsenic compounds when the catalysts are put into contact with such arsenic compounds.

It is, therefore, an object of the invention to provide an economical denitrizing catalyst which retains a high catalytic activity of denitrization over a long period of time.

It is a further object of the invention to provide a denitrizing catalyst which is especially useful for denitrizing waste gases containing a substantial amount of arsenic compounds therein.

It is also an object of the invention to provide a method of catalytic denitrization of waste gases which contain a substantial amount of arsenic compounds therein with effectively suppressing the decrease in denitrizing activity of catalysts.

According to the invention, there is provided a catalyst for denitrizing nitrogen oxides contained in waste gases as defined in claim 1.

It is further essential that the catalyst of the invention contains vanadium concentratedly in the surface layer of the catalyst. The surface layer of the catalyst herein the invention means a layer up to 200 μm , preferably up to 100 μm , in depth from the surface of the catalyst, inclusive of the surface, and vanadium is contained in the surface layer in concentrations of at least 1.5 times as much as the concentrations of vanadium throughout the catalyst. It is likely that under the denitrizing conditions vanadium react with arsenic compounds to form volatile compounds, and is freed from the catalyst. This is one reason why vanadium is concentratedly carried on the surface layer of the catalyst in the invention.

Titanium and vanadium are contained in the catalyst in the form preferably of oxides such as titanium dioxide and vanadium pentoxide, respectively. However, titanium and vanadium may be contained otherwise, for example, in the form of sulfate or nitrate.

Titanium dioxide has a strong affinity for and readily adsorbs thereon arsenic compounds contained in waste gases, and as a result titanium dioxide based denitrizing catalysts are deactivated or poisoned with arsenic compounds within a short period of denitrizing operations. The adsorption of arsenic compounds on titanium dioxide based catalysts is proportional to specific surface area of the titanium dioxide. Therefore, it is desired that the specific surface area of the titanium dioxide in the catalysts is small while not significantly adversely affecting the denitrizing activity of catalysts. From this standpoint, it is preferred that the titanium dioxide contained in the catalyst has large crystallites preferably of 10-25 nm (100-250 Å), however, a slight decrease in denitrizing activity is unavoidably attended by the enlargement of the specific surface area of titanium dioxide. Vanadium incorporated concentratedly in the surface layer of the catalyst makes it possible to very efficiently compensate the decrease of the catalytic activity, so that the catalyst of the invention has a high denitrizing activity.

The denitrizing processes by use of catalysts that contain vanadium are more or less accompanied by the oxidation of sulfur dioxide to sulfur trioxide on account of the catalysis of vanadium in favor of the oxidation. It is generally accepted that the oxidation of sulfur dioxide to sulfur trioxide or conversion rates of sulfur dioxide to sulfur trioxide become larger as the content of vanadium in the catalysts becomes larger.

Therefore, tungsten is contained in the catalyst since tungsten has a high denitrizing catalysis, but is inactive to sulfur dioxide. Tungsten may be contained in the catalyst in weight ratios as defined in claim 1. When the weight ratio is too high, the relative amount of tungsten in the catalyst is too small, so that the tungsten fails to provide a sufficient denitrizing activity with catalysts, whereas when the weight ratio is too small i.e., when the relative amount of tungsten is too large, no additional increase of denitrizing activity is expected, but also the production costs are too expensive. It is preferred that tungsten is incorporated in catalysts in such manners that a part of vanadium is displaced by tungsten especially when the suppression of the oxidation of sulfur dioxide is desired, while a high denitrizing activity is retained.

Tungsten is concentratedly contained in the surface layer of the catalyst in concentration of at least 1.5 times as much as the concentrations of tungsten throughout the catalyst preferably in the form of tungsten trioxide or uniformly distributed throughout the catalyst.

The catalyst of the invention may be produced in any conventional manner known in the art, however, a method is preferred, for example, in which titanium dioxide is first molded into a desired shape, the mold is immersed in or impregnated with aqueous solutions or dispersions of compounds of vanadium, and if desired of tungsten, or both, at the same time or by turns, the mold is taken out of the solutions or dispersions, and then immediately dried in a short time, followed by calcining. Tungsten may be carried on the mold and the mold may be dried and calcined stepwise or by turns. In place of the impregnation or immersion method as above, the solutions or dispersions of compounds of vanadium, and if desired of tungsten, may be coated or sprayed on the titanium dioxide molds. Further, tungsten components may be kneaded together with titanium dioxide, if necessary, and formed into a mold.

The catalyst of the invention may contain clay substances such as montmorillonite, terra abla, bentonite, kaolin, halloysite or sericite; inorganic oxides such as porous silica, alumina, silica, magnesia or zirconia; and heat-resistant inorganic fibers such as glass wool, glass fibers, rock wool or other ceramic fibers, to improve moldability of mixtures of the components in the production of the catalysts, or to provide a high mechanical strength with the catalysts obtained. These additives may be contained in the catalyst in amounts of not more than 50 % by weight based on the weight of the catalyst. Other molding auxiliaries such as binders may be used when molds are formed, when necessary.

The catalyst of the invention has dual micropore structures to have a higher resistance to deactivation or poisoning with arsenic compounds contained in waste gases. It is preferred that the catalyst has micropores of about not less than 5 nm (50 Å) in amounts of 0.25-0.40 ml/g, and micropores of 5-10 nm (50-100 Å) in radius in amounts of 10-40 % by volume and micropores of 100-6000 nm (1000-60000 Å) in radius in amounts of not less than 10 % by volume, respectively, based on the total volume of the micropores of not less than 5 nm (50 Å) in radius.

It has now been found out that the above-mentioned dual micropore structures per se unexpectedly permit the catalyst to retain a high denitrizing activity over a long period of denitrizing operations in the presence of arsenic compounds. Therefore, the catalyst that has not only the dual micropore structures but also vanadium and tungsten concentratedly carried in the surface layer is further improved in resistance to deactivation with arsenic compounds contained in waste gases. Namely, the catalyst retains an initial high denitrizing activity over a long period of operations in the presence of arsenic compounds.

The dual micropore structures are formed by calcining molds which contain therein organic materials which burn out when the molds are calcined. As such organic materials, thermoplastic resins such as polyethylene, polypropylene, polyvinyl alcohol, polyethylene oxide, polyacrylamide or polystyrene, cellulosic materials such as crystalline cellulose or methyl cellulose, urea, ammonium stearate, waxes, organic fibers such as acrylic fibers or silk fibers, lactose, corn starch, wheat flour and the like are usable. Inorganic materials such as ammonium carbonate are also usable.

The catalyst of the invention is honeycombs. Any molding method is adoptable in the production of the catalyst. By way of example, extrusion, tableting or tumbling granulation may be employed depending upon the required properties.

The catalyst of the invention in the form of honeycombs is especially useful for use in denitrizing a large quantity of waste gases that contain a substantial amount of arsenic compounds and sulfur dioxide together with dusts therein. The catalyst in the form of honeycombs has walls of 0.6-1.8 mm, preferably of 1.0-1.4 mm in thickness, and contains titanium, tungsten and vanadium therein in weight ratios of oxides of titanium to oxides of tungsten and oxides of vanadium ranging from 92.5:6.9:0.6 to 82.4:16.5:1.1. In the catalyst titanium is contained in amounts of 70-90 % by weight in terms of titanium dioxide, and the vanadium is concentratedly contained in the surface layer of the catalyst up to 200 µm, preferably up to 100 µm, in depth from the surface of the catalyst in concentrations of at least 1.5 times as much as the concentrations of vanadium throughout the catalyst. The tungsten may be in part displaced by molybdenum. The catalyst may further contain zirconium, preferably in the form of zirconium dioxide, therein. The catalyst also preferably has the dual micropore structure as beforementioned.

According to the invention, there is provided a method for denitrizing nitrogen oxides contained in waste gases which contains a substantial amount of arsenic compounds as well therein, which comprises putting the waste gas into contact with the catalyst as described hereinbefore in the presence of a reducing gas, at elevated temperatures, thereby to convert the nitrogen oxides, which include nitrogen monoxide, dinitrogen trioxide, nitrogen dioxide and nitrogen hexaoxide, into innocuous compounds.

The use of the catalyst of the invention for denitrizing nitrogen oxides in waste gases permits the retention of a high initial denitrizing activity of the catalyst even when the waste gases contain a substantial amount of arsenic compounds therein.

In the method of the invention, the reducing gas may be either hydrogen, hydrocarbons, carbon monoxide or ammonia, however, ammonia is most preferred as described hereinbefore. The amount of the reducing gases used is usually not more than 10 times, and is preferably in the range of 0.2-2 times, as much as the stoichiometric amount needed to reduce the nitrogen oxides contained in waste gases. When ammonia gas is used, it is preferred that the amount is not more than the stoichiometric amount needed to reduce the nitrogen oxides contained in waste gases to prevent sec-

ondary pollution due to unreacted ammonia. The most advantageous amount of ammonia is in the range of 0.2-1.0 times as much as the stoichiometric amount needed to reduce the nitrogen oxides in waste gases.

In the method of the invention, the waste gases are put into contact with the catalyst preferably at temperatures of 100-550° C, more preferably of 200-500°C, most preferably of 250-400°C, in the presence of a reducing gas. Usually the waste gas is passed through as a mixture with a reducing gas a reactor having the catalysts fitted therein. The space velocity of the gas mixture is preferably in the range of 1000-100000 hr⁻¹, more preferably 2000-50000 hr⁻¹, most preferably 3000-30000 hr⁻¹, at pressures of 1.01-10.1 bar (1-10 kg/cm²).

The catalyst and method of the invention are suitably applicable to denitrizing of waste gas which contains nitrogen oxides and arsenic compounds, and they are especially useful when used for denitration of combustion waste gases which contain 100-1000 ppm of nitrogen oxides, mainly nitrogen monoxide, 200-2000 ppm of sulfur oxides, mainly sulfur dioxide, 1-10 % by volume of oxygen, 5-20 % by volume of carbon dioxide, 5-20 % by volume of water vapor, and a substantial amount of arsenic compounds, i.e. not less than 0.001 ppm. The catalyst and method of the invention are most useful when they are used for denitration of combustion waste gases from coal-fired boilers which contain arsenic oxides, mainly diarsenic trioxide, in amounts of 0.01-1.0 ppm since when the conventional catalysts are used to denitrize such waste gases, they are deactivated within a very short period of time. However, the method of the invention is not specifically limited in the concentration of arsenic oxides in waste gases.

The invention will be more easily understood with reference to the following examples, which however are intended to illustrate the invention only and are not to be construed as limiting the scope of the invention.

Example 1

Metatitanic acid which was obtained as an intermediate in the production of titanium dioxide by a sulfuric acid process was neutralized, filtered and washed, to provide metatitanic acid cake. An amount of 8 kg of 67.5 % aqueous nitric acid solution was added to 800 kg (in terms of titanium dioxide) of the metatitanic acid cake to partially peptize the metatitanic acid. The resultant sol solution was spray-dried, and then the resultant particles were calcined at temperatures of 450° C for 3 hours. After cooling, the particles were pulverized to fine powders of titanium dioxide of 2 µm in average particle size.

An amount of 300 lit. of an aqueous solution of monoethanol amine containing therein 100 kg of ammonium paratungstate, 50 kg of polyvinyl alcohol and 100 kg of glass chopped strands of 5 mm in fibers length and 9 µm in diameter were added to 800 kg of the titanium dioxide powders together with about 100 lit., and the resultant mixture was kneaded.

The kneaded mixture was then molded into a honeycomb structure by use of a screw extruder provided with a honeycomb forming nozzle. The thus obtained mold was left standing for drying for sufficient period of time, and then air dried at 100°C for 5 hours. The mold was then cut at both axial ends to a predetermined length, and calcined at 450°C for 3 hours in an electric oven, to provide a honeycomb mold of 7.4 mm in cell pitch, 1.35 mm in wall thickness, 150 mm x 150 mm in outer diameter, 500 mm in axial length and 5.9 mm in equivalent diameter.

An amount of 19.2 kg of oxalic acid and 7.7 kg of ammonium metavanadate were added to water to form an aqueous solution in an amount of 40 lit. or in concentration of 150 g/l of vanadium pentoxide, which was then diluted to a concentration of 17.9 g/l with water.

The honeycomb mold obtained as above was immersed in the above diluted ammonium metavanadate solution at 60°C, and immediately after taking the mold out of the solution, the mold was heated to 100°C in 1 hour, dried at 100 ° C for 5 hours, and calcined at 450°C for 3 hours, to provide a honeycomb structure catalyst.

The catalyst was found to contain TiO₂, V₂O₅ and WO₃ in amounts of 79.8 %, 0.6 % and 8.9 % by weight based on the catalyst, respectively, with weight ratios TiO₂/WO₃/V₂O₅ of 89.4/10.0/0.7.

Reference Example 1

The same honeycomb mold as in Example 1 containing therein titanium dioxide and tungsten trioxide was immersed in the same vanadium solution at room temperatures, taken out of the solution, air-dried at room temperatures for 2.5 hours, heated to 100°C in 5 hours, dried at 100°C for 5 hours, and was calcined at 450°C for 3 hours, to provide a honeycomb structure catalyst.

The catalyst was found to contain TiO₂, V₂O₅ and WO₃ in amounts of 79.8 %, 0.6 % and 8.9 % by weight based on the catalyst, respectively, with weight ratios TiO₂/WO₃/V₂O₅ of 89.4/10.0/0.7.

Example 2

The same honeycomb mold as in Example 1 containing therein titanium dioxide and tungsten trioxide was immersed in a 240.9 g/l aqueous solution of zirconium oxychloride at room temperatures, dried in the same manner as in Example 1, and then calcined at 450°C for 3 hours.

After cooling, the mold was immersed in a 17.9 g/l aqueous solution of vanadium at 60°C, dried in the same manner as in Example 1, and then calcined at 450°C for 3 hours.

The catalyst was found to contain TiO_5 , V_2O_5 , WO_3 and ZrO_2 in amounts of 75.8 %, 0.6 %, 8.4 % and 4.5 % by weight based on the catalyst, respectively, with weight ratios $\text{TiO}_2/\text{WO}_3/\text{ZrO}_2/\text{V}_2\text{O}_5$ of 84.9/9.4/5.0/0.7.

Example 3

An amount of 300 lit. of an aqueous solution of monoethanol amine containing therein 100 kg of ammonium paratungstate, 50 kg of polyvinyl alcohol, 50 g of a thermoplastic resin and 100 kg of glass chopped strands of 5 mm in fibers length and 9 μm in diameter were added to 800 kg of the same fine powders of titanium dioxide of 2 μm in average particle size together with about 100 lit. of water, and the resultant mixture was kneaded.

The kneaded mixture was then molded into a honeycomb structure by use of a screw extruder provided with a honeycomb forming nozzle. The thus obtained mold was left standing for drying for sufficient period of time, and then air dried at 100°C for 5 hours. The mold was then cut at both axial ends to a predetermined length, and calcined at 450°C for 3 hours in an electric oven, to provide a honeycomb mold of 7.4 mm in cell pitch, 1.35 mm in wall thickness, 150 mm x 150 mm in outer diameter, 500 mm in axial length and 5.9 mm in equivalent diameter.

An amount of 19.2 kg of oxalic acid and 7.7 kg of ammonium metavanadate were added to water to form an aqueous solution in an amount of 40 lit. or in concentration of 150 g/l of vanadium pentoxide, which was then diluted to a concentration of 21.9 g/l with water.

The honeycomb mold obtained as above was immersed in the above diluted vanadium solution at 60°C, and immediately after taking the mold out of the solution, the mold was heated to 100°C in 1 hour, dried at 100°C for 5 hours, and calcined at 450°C for 3 hours, to provide a honeycomb structure catalyst with a dual micropore structure.

The catalyst was found to contain TiO_2 , V_2O_5 and WO_3 in amounts of 79.6 %, 0.7 % and 8.9 % by weight based on the catalyst, respectively, with weight ratios $\text{TiO}_2/\text{WO}_3/\text{V}_2\text{O}_5$ of 89.0/10.0/0.8. Further the pore volume and pore size distribution of the catalysts were measured with a mercury porosimeter. Fig. 1 shows a micropore distribution and cumulative micropore volume of the catalyst.

The catalyst was found to have micropores of not less than 5 nm (50 Å) in radius in amounts of 0.31 ml/g, and about 36 % by volume of micropores of 5-10 nm (50-100 Å) in radius and about 17 % by volume of micropores of 100-6000 nm (1000-6000 Å) based on the pore volume of the micropores of not less than (50 Å) in radius.

The concentration distributions of vanadium in the catalysts prepared in Example 1 and Reference Example 1 were measured by use of an X-ray microanalyzer (ASM-SX by Shimadzu K.K., Japan), and the results are shown in Figs. 2 and 3, respectively. As apparent, the catalyst of Example 1 was found to contain vanadium concentratedly in the surface layer, whereas the catalyst of Reference Example 1 was found to contain vanadium in substantially the same concentration throughout the catalyst.

Further the concentrations of vanadium in the entire bodies of the catalysts and in the surface layer up to 200 μm in depth from the surface were determined by chemical analysis, and the results are shown in Table 1.

TABLE 1

Catalysts	Concentrations of Vanadium (% by weight)	
	in Entire Bodies	in Surface Layers
Example 1	0.60	1.4
Example 2	0.60	1.5
Example 3	0.72	1.9
Reference 1	0.60	0.6

The catalysts prepared in Examples 1 to 3, and Reference Example 1 were cut into honeycombs of 300 mm in length and having nine openings extending therethrough in 3 x 3 cells, respectively.

At first, a gas mixture composed of 200 ppm of nitrogen oxides, 200 ppm of ammonia, 4 % by volume of oxygen, 10 % by volume of water vapor, 12 % by volume of carbon dioxide, 800 ppm of sulfur dioxide and the balance nitrogen was put into contact with the individual catalyst at 380°C at a space velocity of 4700hr^{-1} for a short period of time to determine initial denitrizing rates π_1 of the catalysts.

Then a gas mixture composed of 200 ppm of nitrogen oxides, 200 ppm of ammonia, 4 % by volume of oxygen, 10 % by volume of water vapor, 12 % by volume of carbon dioxide, 800 ppm of sulfur dioxide, 25 ppm of diarsenic trioxide vapor, and the balance nitrogen was put into contact with the individual catalyst at 380°C at a space velocity of 4700hr^{-1} for 5 hours, and denitrizing rates π_2 of the catalyst and SO_2 conversions were measured.

The denitrizing rate is defined by $((\text{NO}_x \text{ concentration at the inlet of a reactor}) - (\text{NO}_x \text{ concentration at the outlet of a reactor})) / (\text{NO}_x \text{ concentration at the inlet of a reactor}) \times 100 (\%)$. The SO_2 conversion is defined as $((\text{SO}_2 \text{ concentration at the inlet of a reactor}) - (\text{SO}_2 \text{ concentration at the outlet of a reactor})) / (\text{SO}_2 \text{ concentration at the inlet of a reactor}) \times 100 (\%)$. The results are shown in Table 2.

5 Further over-all coefficients of reaction velocity K and retentions of denitrizing activity R were calculated. K is represented by $-(1/2)(S.V. \ln(1 - \pi)) / O.S.$ wherein $S.V.$ is a space velocity of the gas put into contact with the catalyst, and $O.S.$ is an outer surface area of the catalyst used per cubic meter, which was found $427 \text{ m}^2/\text{m}^3$ with all the catalysts. R is represented by $((1n(1 - \pi_2) / 1n(1 - \pi_1)) \times 100 (\%))$. The results are shown in Table 2.

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TABLE 2

Catalysts	Denitrizing Rates (%)		Over-all Coefficients of Reaction Velocity		Retentions of Denitrizing Activity (%)		SO ₂ Conversions (%)
	η_1	η_2	K_1	K_2	R	R	
Example 1	97.0	89.7	38.6	25.0	64.8	64.8	0.7
Example 2	97.9	91.9	42.5	27.6	64.9	64.9	0.7
Example 3	98.2	93.9	44.2	30.8	69.7	69.7	0.8
Reference	96.2	82.6	36.0	19.2	53.3	53.3	0.6

Notes: 1) $K = -\frac{1}{2} \times \frac{S.V.}{0.5} \ln(1 - \eta)$ wherein S.V. is a space velocity of the gas, and O.S. is an outer surface area of the catalyst used per m³ (427 m²/m³).

2) Retentions of denitrizing activity are defined as $\frac{\ln(1 - \eta_2)}{\ln(1 - \eta_1)} \times 100 (\%)$.

Claims

Claims for the following Contracting States : BE, DE, FR, GB, IT, NL, SE

1. A catalyst in the form of honeycombs for denitrizing waste gases that contain a substantial amount of arsenic compounds and sulfur dioxide together with dusts therein, which comprises a honeycomb structure molded with titanium dioxide, wherein the honeycomb structure comprises titanium, tungsten and vanadium therein in weight ratios of oxides of titanium to oxides of tungsten and oxides of vanadium ranging from 92.5:6.9:0.6 to 82.4:16.5:1.1, the titanium being contained in the catalyst in amounts of 70-90 % by weight in terms of titanium dioxide, and the vanadium being concentratedly contained in the surface layer of the catalyst up to 200 μm in depth from the surface of the catalyst in concentrations of at least 1.5 times as much as the concentrations of vanadium throughout the catalyst, the honeycombs having walls of 0.6-1.8 mm in thickness, wherein the catalyst has micropores of not less than 5 nm (50 Å) in amounts of 0.25-0.40 ml/g and micropores of 5-10 nm (50-100 Å) in radius in amounts of 10-40 % by volume and micropores of 100-6000 nm (1000-60000 Å) in radius in amounts of not less than 10 % by volume, respectively, based on the total volume of the micropores of not less than 5 nm (50 Å) in radius.
2. The catalyst as claimed in claim 1, wherein the vanadium is concentratedly contained in the surface layer of the catalyst up to 100 μm in depth from the surface of the catalyst in concentrations of at least 1.5 times as much as the concentrations of vanadium throughout the catalyst, and the honeycombs have walls of 1.0-1.4 mm in the thickness.
3. The catalyst as claimed in claim 2, wherein the tungsten is in part replaced by molybdenum.
4. The catalyst as claimed in claims 1 to 3, wherein the titanium dioxide is molded together with a clay substance, inorganic oxide selected from porous silica, alumina, magnesia, or zirconia and heat resistant inorganic fibers.
5. A method for denitrizing nitrogen oxides contained in waste gases which contain a substantial amount of arsenic or arsenic compounds therein, which comprises putting the waste gases into contact with a catalyst according to claims 1 to 4 in the presence of a reducing gas at elevated temperatures.
6. The method as claimed in claim 5 wherein the reducing gas is ammonia.
7. The method as claimed in claim 5 wherein the waste gases contain arsenic or arsenic compounds in amounts of not less than 0.001 ppm.
8. The method as claimed in claim 5 wherein the waste gases contain arsenic or arsenic compounds in amounts of not less than 0.01 ppm.
9. The method as claimed in claim 5 wherein the temperature is in the range of 100-550 °C.

Claims for the following Contracting State : AT

1. A process for preparing a catalyst in the form of honeycombs for denitrizing waste gases that contain a substantial amount of arsenic compounds and sulfur dioxide together with dusts therein, which comprises a honeycomb structure molded with titanium dioxide, wherein the honeycomb structure which comprises titanium, tungsten and vanadium therein in weight ratios of oxides of titanium to oxides of tungsten and oxides of vanadium ranging from 92.5:6.9:0.6 to 82.4:16.5:1.1, the titanium being contained in the catalyst in amounts of 70-90 % by weight in terms of titanium dioxide, and the vanadium being concentratedly contained in the surface layer of the catalyst up to 200 μm in depth from the surface of the catalyst in concentrations of at least 1.5 times as much as the concentrations of vanadium throughout the catalyst, the honeycombs having walls of 0.6-1.8 mm in thickness, wherein the catalyst has micropores of not less than 5 nm (50 Å) in amounts of 0.25-0.40 ml/g and micropores of 5-10 nm (50-100 Å) in radius in amounts of 10-40 % by volume and micropores of 100-6000 nm (1000-60000 Å) in radius in amounts of not less than 10 % by volume, respectively, based on the total volume of the micropores of not less than 5 nm (50 Å) in radius, by molding titanium dioxide first into the desired shape, immersing in or impregnating with aqueous solutions or dispersions of compounds of vanadium and tungsten and optionally zirconium, or both, at the same time or by turns, or in place of the impregnation or immersion coating or spraying the solutions or dispersions of compounds of vanadium on the titanium dioxide molds or kneading the tungsten component together with titanium dioxide and, if necessary, forming into the mold.

2. The process for preparing a catalyst as claimed in claim 1, wherein the vanadium is concentratedly contained in the surface layer of the catalyst up to 100 µm in depth from the surface of the catalyst in concentrations of at least 1.5 times as much as the concentrations of vanadium throughout the catalyst, and the honeycombs have walls of 1.0-1.4 mm in the thickness.
3. The process for preparing a catalyst as claimed in claim 2, wherein the tungsten is in part replaced by molybdenum.
4. The process for preparing a catalyst as claimed in claims 1 to 3, wherein the titanium dioxide is molded together with a clay substance, inorganic oxide selected from porous silica, alumina, magnesia, or zirconia and heat resistant inorganic fibers.
5. A method for denitrizing nitrogen oxides contained in waste gases which contain a substantial amount of arsenic or arsenic compounds therein, which comprises putting the waste gases into contact with a catalyst obtained by the method of claims 1 to 4 in the presence of a reducing gas at elevated temperatures.
6. The method as claimed in claim 5 wherein the reducing gas is ammonia.
7. The method as claimed in claim 5 wherein the waste gases contain arsenic or arsenic compounds in amounts of not less than 0.001 ppm.
8. The method as claimed in claim 5 wherein the waste gases contain arsenic or arsenic compounds in amounts of not less than 0.01 ppm.
9. The method as claimed in claim 5 wherein the temperature is in the range of 100-550 °C.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : BE, DE, FR, GB, IT, NL, SE

1. Katalysator in Wabenform zum Denitrieren von Abgasen, die eine wesentliche Menge von Arsenverbindungen und Schwefeldioxid zusammen mit Stäuben enthalten, umfassend eine mit Titandioxid geformte Wabenstruktur, wobei die Wabenstruktur Titan, Wolfram und Vanadium in Gewichtsverhältnissen der Oxide von Titan zu Oxiden von Wolfram und Oxiden von Vanadium im Bereich von 92,5 : 6,9 : 0,6 bis 82,4 : 16,5 : 1,1 umfaßt, wobei das Titan in Mengen von 70-90 Gew. -%, ausgedrückt als Titandioxid, im Katalysator enthalten ist und das Vanadium in der Oberflächenschicht des Katalysators in bis zu 200 µm Tiefe von der Oberfläche des Katalysators in Konzentrationen von wenigstens dem 1,5 fachen der Konzentrationen von Vanadium über den gesamten Katalysator konzentriert enthalten ist, wobei die Waben Wände von 0,6-1,8 mm Dicke haben, wobei der Katalysator Mikroporen von nicht weniger als 5 nm (50 Å) in Mengen von 0,25-0,40 ml/g und Mikroporen mit einem Radius von 5-10 nm (50-100 Å) in Mengen von 10-40 Vol. -% bzw. Mikroporen mit einem Radius von 100-6000 nm (1000-60000 Å) in Mengen von nicht weniger als 10 Vol.-% aufweist, bezogen auf das Gesamtvolumen der Mikroporen mit einem Radius von nicht weniger als 5 nm (50 Å).
2. Katalysator nach Anspruch 1, wobei das Vanadium in der Oberflächenschicht des Katalysators in bis zu 100 µm Tiefe von der Oberfläche des Katalysators in Konzentrationen von wenigstens dem 1,5 fachen der Konzentrationen von Vanadium über den gesamten Katalysator konzentriert enthalten ist und die Waben Wände von 1,0-1,4 mm Dicke haben.
3. Katalysator nach Anspruch 2, wobei das Wolfram teilweise durch Molybdän ersetzt ist.
4. Katalysator nach Anspruch 1 bis 3, wobei das Titandioxid zusammen mit einer Tonsubstanz, einem anorganischen Oxid, das aus porösem Siliciumoxid, Aluminiumoxid, Magnesiumoxid oder Zirkoniumoxid ausgewählt ist, und hitzebeständigen anorganischen Fasern geformt ist.
5. Verfahren zum Denitrieren von Stickoxiden, die in Abgasen enthalten sind, welche eine wesentliche Menge von Arsen oder Arsenverbindungen enthalten, umfassend das In-Kontakt-Bringen der Abgase mit einem Katalysator nach Anspruch 1-4 in Gegenwart eines reduzierenden Gases bei erhöhten Temperaturen.
6. Verfahren nach Anspruch 5, wobei das reduzierende Gas Ammoniak ist.

7. Verfahren nach Anspruch 5, wobei die Abgase Arsen oder Arsenverbindungen in Mengen von nicht weniger als 0,001 ppm enthalten.
8. Verfahren nach Anspruch 5, wobei die Abgase Arsen oder Arsenverbindungen in Mengen von nicht weniger als 0,01 ppm enthalten.
9. Verfahren nach Anspruch 5, wobei die Temperatur im Bereich von 100-550°C liegt.

Patentansprüche für folgenden Vertragsstaat : AT

1. Verfahren zur Herstellung eines Katalysators in Wabenform zum Denitrieren von Abgasen, die eine wesentliche Menge von Arsenverbindungen und Schwefeldioxid zusammen mit Stäuben enthalten, der eine mit Titandioxid geformte Wabenstruktur umfaßt, wobei die Wabenstruktur Titan, Wolfram und Vanadium in Gewichtsverhältnissen der Oxide von Titan zu Oxiden von Wolfram und Oxiden von Vanadium im Bereich von 92,5 : 6,9 : 0,6 bis 82,4 : 16,5 : 1,1 umfaßt, wobei das Titan in Mengen von 70-90 Gew. -%, ausgedrückt als Titandioxid, im Katalysator enthalten ist und das Vanadium in der Oberflächenschicht des Katalysators in bis zu 200 µm Tiefe von der Oberfläche des Katalysators in Konzentrationen von wenigstens dem 1,5 fachen der Konzentrationen von Vanadium über den gesamten Katalysator konzentriert enthalten ist, wobei die Waben Wände von 0,6-1,8 mm Dicke haben, wobei der Katalysator Mikroporen von nicht weniger als 5 nm (50 Å) in Mengen von 0,25-0,40 ml/g und Mikroporen mit einem Radius von 5-10 nm (50-100 Å) in Mengen von 10-40 Vol. -% bzw. Mikroporen mit einem Radius von 100-6000 nm (1000-60000 Å) in Mengen von nicht weniger als 10 Vol. -% aufweist, bezogen auf das Gesamtvolumen der Mikroporen mit einem Radius von nicht weniger als 5 nm (50 Å), wobei man Titandioxid zuerst durch Formgießen in die gewünschte Form bringt, gleichzeitig oder nacheinander in wäßrige Lösungen oder Dispersionen von Verbindungen von Vanadium und Wolfram und gegebenenfalls Zirkonium eintaucht oder damit imprägniert oder beides oder anstelle des Imprägnierens oder Eintauchens die Lösungen oder Dispersionen von Verbindungen von Vanadium auf die Titandioxidformen aufträgt oder sprüht oder die Wolframkomponente zusammen mit Titandioxid knetet und, falls notwendig, in die Gießform bildet.
2. Verfahren zur Herstellung eines Katalysators nach Anspruch 1, wobei das Vanadium in der Oberflächenschicht des Katalysators in bis zu 100 µm Tiefe von der Oberfläche des Katalysators in Konzentrationen von wenigstens dem 1,5 fachen der Konzentrationen von Vanadium über den gesamten Katalysator konzentriert enthalten ist und die Waben Wände von 1,0-1,4 mm Dicke haben.
3. Verfahren zur Herstellung eines Katalysators nach Anspruch 2, wobei das Wolfram teilweise durch Molybdän ersetzt ist.
4. Verfahren zur Herstellung eines Katalysators nach Anspruch 1 bis 3, wobei das Titandioxid zusammen mit einer Tonsubstanz, einem anorganischen Oxid, das aus porösem Siliciumoxid, Aluminiumoxid, Magnesiumoxid oder Zirkoniumoxid ausgewählt ist, und hitzebeständigen anorganischen Fasern geformt wird.
5. Verfahren zum Denitrieren von Stickoxiden, die in Abgasen enthalten sind, welche eine wesentliche Menge von Arsen oder Arsenverbindungen enthalten, umfassend das In-Kontakt-Bringen der Abgase mit einem Katalysator, der nach dem Verfahren nach Anspruch 1-4 erhalten wurde, in Gegenwart eines reduzierenden Gases bei erhöhten Temperaturen.
6. Verfahren nach Anspruch 5, wobei das reduzierende Gas Ammoniak ist.
7. Verfahren nach Anspruch 5, wobei die Abgase Arsen oder Arsenverbindungen in Mengen von nicht weniger als 0,001 ppm enthalten.
8. Verfahren nach Anspruch 5, wobei die Abgase Arsen oder Arsenverbindungen in Mengen von nicht weniger als 0,01 ppm enthalten.
9. Verfahren nach Anspruch 5, wobei die Temperatur im Bereich von 100-550°C liegt.

Revendications

Revendications pour les Etats contractants suivants : BE, DE, FR, GB, IT, NL, SE

- 5 1. Catalyseur sous la forme de nid d'abeille pour dénitrifier des gaz de rejet qui contiennent une quantité notable de composés d'arsenic et de dioxyde de soufre avec des poussières dedans, qui comprend une structure de nid d'abeille moulée avec du dioxyde de titane, dans lequel la structure de nid d'abeille comprend du titane, du tungstène et du vanadium en rapports pondéraux d'oxydes de titane aux oxydes de tungstène et oxydes de vanadium allant de 92,5: 6,9 : 0,6 à 82,4:16,5: 1,1, le titane étant contenu dans le catalyseur dans des proportions de 70-90% en poids exprimé en dioxyde de titane et, le vanadium étant contenu de façon concentrée dans la couche superficielle du catalyseur jusqu'à 200 µm en profondeur à partir de la surface du catalyseur en des concentrations d'au moins 1,5 fois les concentrations de vanadium à travers le catalyseur, le nid d'abeille ayant des cloisons de 0,6-1,8 mm d'épaisseur, dans lequel le catalyseur a des micropores qui ne sont pas inférieurs à 5 nm (50 Å) en quantités de 0,25-0,40 ml/g et des micropores de 5-10 nm (50-100 Å) de rayon dans des proportions de 10 - 40% en volume et des micropores de 100-6000 nm (1000-60000 Å) de rayon dans des proportions qui ne sont pas inférieures à 10% en volume, respectivement, par rapport au volume total des micropores qui ne sont pas inférieurs à 5 nm (50 Å) de rayon.
- 10 2. Catalyseur selon la revendication 1, dans lequel le vanadium est contenu de façon concentrée dans la couche superficielle du catalyseur jusqu'à 100 µm en profondeur à partir de la surface du catalyseur dans des concentrations d'au moins 1,5 fois les concentrations de vanadium à travers tout le catalyseur et le nid d'abeille a des parois de 1,0-1,4 mm d'épaisseur.
- 25 3. Catalyseur selon la revendication 2, dans lequel le tungstène est en partie remplacé par le molybdène.
4. Catalyseur selon les revendications 1 à 3, dans lequel le dioxyde de titane est moulé ensemble avec une substance argileuse, l'oxyde minéral étant choisi à partir de silice poreuse, d'alumine, de magnésie ou d'oxyde de zirconium et de fibres minérales résistant à la chaleur.
- 30 5. Procédé de dénitrification d'oxydes d'azote contenu dans des gaz de rejet, qui contiennent une proportion notable d'arsenic ou de composés d'arsenic, qui consiste à mettre les gaz de rejet en contact avec un catalyseur selon les revendications 1 à 4, en présence d'un gaz réducteur à des températures élevées.
- 35 6. Procédé selon la revendication 5, dans lequel le gaz réducteur est l'ammoniac.
7. Procédé selon la revendication 5, dans lequel les gaz de rejet contiennent de l'arsenic ou des composés d'arsenic dans des proportions qui ne sont pas inférieures à 0,001 ppm.
- 40 8. Procédé selon la revendication 5 dans lequel les gaz de rejet contiennent de l'arsenic ou des composés d'arsenic dans des proportions qui ne sont pas inférieures à 0,01 ppm.
9. Procédé selon la revendication 7, dans lequel la température se situe dans la plage allant de 100-550°C.

Revendications pour l'Etat contractant suivant : AT

- 45 1. Procédé pour préparer un catalyseur sous la forme de nid d'abeille pour dénitrifier des gaz de rejet qui contiennent une quantité notable de composés d'arsenic et de dioxyde de soufre avec des poussières dedans, qui comprend une structure de nid d'abeille moulée avec du dioxyde de titane, dans lequel la structure de nid d'abeille qui comprend du titane, du tungstène, et du vanadium en rapports pondéraux d'oxydes de titane aux oxydes de tungstène et oxydes de vanadium allant de 92,5: 6,9 : 0,6 à 82,4:16,5:1,1, le titane étant contenu dans le catalyseur dans des proportions de 70-90% en poids exprimé en dioxyde de titane et, le vanadium étant contenu, de façon concentrée, dans la couche superficielle du catalyseur jusqu'à 200µm en profondeur à partir de la surface du catalyseur en des concentrations d'au moins 1,5 fois les concentrations de vanadium à travers le catalyseur, le nid d'abeille ayant des cloisons de 0,6 - 1,8mm d'épaisseur, dans lequel le catalyseur a des micropores qui ne sont pas inférieurs à 5 nm (50 Å) en quantités de 0,25-0,40 ml/g et, des micropores de 5 - 10 nm (50 à 100 Å) de rayon dans des proportions de 10 - 40 % en volume et des micropores de 100-6000 nm (1000-60000 Å) de rayon dans des proportions qui ne sont pas inférieures à 10% en volume, respectivement, par rapport au volume total des micropores qui ne sont pas inférieurs à 5nm (50 Å) de rayon, consistant à mouler tout d'abord l'oxyde de titane en une forme souhaitée, à l'immerger dans ou à l'imprégner avec des solutions aqueuses ou des dispersions de composés de vanadium et

de tungstène et, éventuellement, de zirconium, ou les deux, à la fois ou alternativement, ou au lieu de l'imprégnation ou de l'immersion, à revêtir, ou à pulvériser des solutions ou des dispersions de composés de vanadium sur, les matrices de dioxyde de titane ou à malaxer ensemble le constituant de tungstène avec le dioxyde de titane et, si nécessaire, à les mettre sous forme d'une matrice.

2. Procédé pour préparer un catalyseur selon la revendication 1, dans lequel le vanadium est contenu de façon concentrée dans la couche superficielle du catalyseur jusqu'à 100µm en profondeur à partir de la surface du catalyseur dans des concentrations d'au moins 1,5 fois les concentrations de vanadium à travers tout le catalyseur et le nid d'abeille a des parois de 1,0-1,4 mm d'épaisseur.
3. Procédé pour préparer un catalyseur selon la revendication 2, dans lequel le tungstène est en partie remplacé par le molybdène.
4. Procédé pour préparer un catalyseur selon les revendications 1 à 3, dans lequel le dioxyde de titane est moulé avec une substance argileuse, l'oxyde minéral étant choisi à partir de silice poreuse, d'alumine, de magnésie ou d'oxyde de zirconium et de fibres minérales résistant à la chaleur.
5. Procédé de dénitrification d'oxydes d'azote contenus dans des gaz de rejet qui contiennent une proportion notable d'arsenic ou de composés d'arsenic, qui consiste à mettre les gaz de rejet en contact avec un catalyseur obtenu selon les revendications de procédé 1 à 4, en présence d'un gaz réducteur à des températures élevées.
6. Procédé selon la revendication 5 dans lequel le gaz réducteur est l'ammoniac.
7. Procédé selon la revendication 5 dans lequel les gaz de rejet contiennent de l'arsenic ou des composés d'arsenic dans des proportions qui ne sont pas inférieures à 0,001 ppm.
8. Procédé selon la revendication 5 dans lequel les gaz de rejet contiennent de l'arsenic ou des composés d'arsenic dans des proportions qui ne sont pas inférieures à 0,01 ppm.
9. Procédé selon la revendication 5 dans lequel la température est située dans la plage allant de 100-550°C.

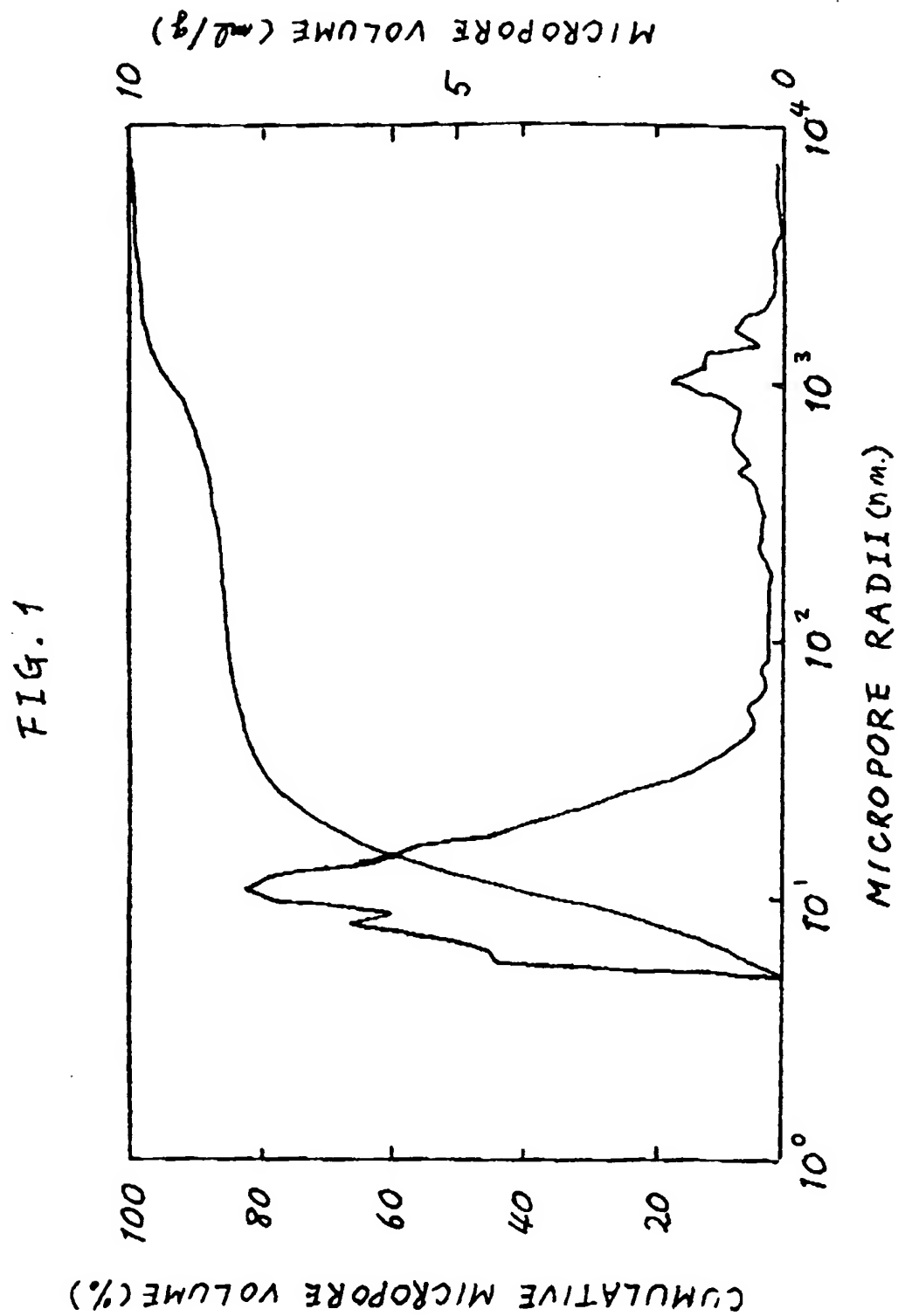


FIG. 2

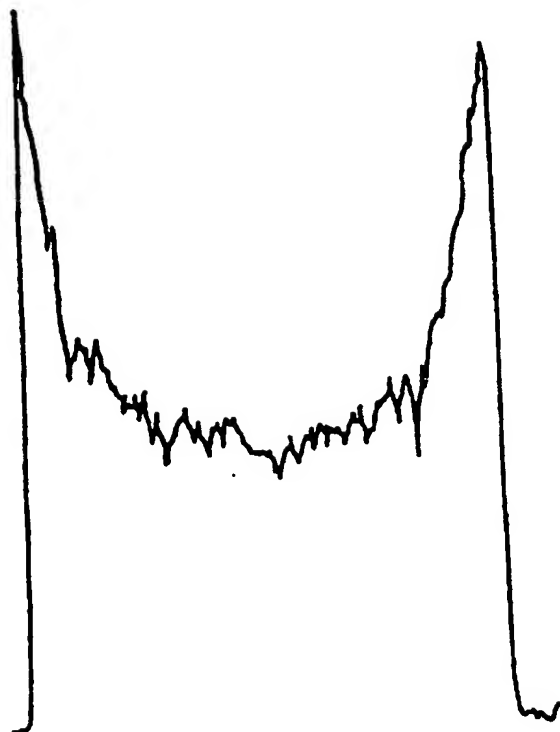


FIG. 3

